Chapter 34 – THE MULTI-COMPONENT RANDOM PHASE APPROXIMATION

1. COMPRESSIBLE POLYMER MIXTURE

Consider a homogeneous mixture consisting of m polymer components. Components are homopolymers, blocks in copolymers or solvents. Within the Random Phase Approximation formalism (De Gennes, 1979; Benmouna et al, 1987; Akcasu-Tombakoglu, 1990) for compressible mixtures, the scattering cross section for this system is expressed in general terms as follows:

$$\frac{d\Sigma(Q)}{d\Omega} = \underline{\rho}^T . \underline{\underline{S}}(Q) . \underline{\rho} .$$

(1)

Here $\underline{\underline{S}}(Q)$ is an m*m matrix and $\underline{\rho}$ is a column vector containing the m scattering length densities. $\underline{\rho}^T$ is the "transpose" row vector. The fully interacting scattering factors $\underline{\underline{S}}(Q)$ are expressed in terms of the non-interacting (so called "bare") scattering factors $\underline{\underline{S_0}}(Q)$ and inter-monomer interaction potentials $\underline{\underline{W}}$ as follows:

$$\underline{\underline{S}}^{-1}(Q) = \underline{\underline{S_0}}^{-1}(Q) + \frac{\underline{\underline{W}}}{k_B T} .$$

(2)

This equation can easily be derived using the linear response approach without the incompressibility constraint. The incompressibility condition simplifies things as described next.

2. INCOMPRESSIBLE POLYMER MIXTURE

Now consider one of the m polymer components as the "background" component. This can be a homopolymer or a solvent. It cannot be a block that belongs to a copolymer. Imposing the incompressibility condition eliminates the background component. This leaves (m-1) explicit components. Even though this formalism is general, it is described here explicitly for four components (m = 4). Component 4 is referred to as the "background" component. The Random Phase Approximation formalism for incompressible mixtures yields the following macroscopic scattering cross section:

$$\frac{d\Sigma(Q)}{d\Omega} = \underline{\Delta\rho}^T . \underline{\underline{S}}(Q) . \underline{\Delta\rho}$$

(3)

$$= \Delta\rho_1^2 S_{11}(Q) + \Delta\rho_2^2 S_{22}(Q) + \Delta\rho_3^2 S_{33}(Q) + 2\Delta\rho_1\Delta\rho_2 S_{12}(Q) + 2\Delta\rho_1\Delta\rho_3 S_{13}(Q) + 2\Delta\rho_2\Delta\rho_3 S_{23}(Q)$$

In this general RPA formalism (Akcasu-Tombakoglu, 1990; Hammouda, 1993) $\underline{\underline{S}}(Q)$ is an (m-1)*(m-1) matrix and $\underline{\Delta\rho}$ is an (m-1) column vector for the scattering length density differences (the scattering length density of the background component is subtracted for each component). The new general relation follows:

$$\underline{\underline{S}}^{-1}(Q) = \underline{\underline{S}}_0^{-1}(Q) + \underline{\underline{v}}(Q) \qquad (4)$$

$$\underline{\underline{S}}(Q) = \left(\underline{\underline{1}} + \underline{\underline{S}}_0(Q).\underline{\underline{v}}(Q)\right)^{-1} \underline{\underline{S}}_0(Q).$$

The "bare" scattering factor $\underline{\underline{S}}_0(Q)$ is a diagonal matrix for homopolymer blends and homopolymer solutions. Mixtures containing copolymers contain off-diagonal elements.

$$\underline{\underline{S}}_0(Q) = \begin{bmatrix} S_{11}^0(Q) & S_{12}^0(Q) & S_{13}^0(Q) \\ S_{21}^0(Q) & S_{22}^0(Q) & S_{23}^0(Q) \\ S_{31}^0(Q) & S_{32}^0(Q) & S_{33}^0(Q) \end{bmatrix}. \qquad (5)$$

The interaction matrix is expressed in terms of the bare scattering factor for the background component and the various Flory-Huggins interaction parameters.

$$v_{ii}(Q) = \frac{1}{S_{44}^0(Q)} - 2\frac{\chi_{i4}}{v_0} \text{ for i = 1,2,3} \qquad (6)$$

$$v_{ij}(Q) = \frac{1}{S_{44}^0(Q)} + \frac{\chi_{ij}}{v_0} - \frac{\chi_{i4}}{v_0} - \frac{\chi_{j4}}{v_0} \text{ for i,j = 1,2,3.}$$

The various scattering length densities for the various components are given by:

$$\Delta\rho_i = \rho_i - \rho_4 \text{ for i = 1,2,3.} \qquad (7)$$

The incompressibility assumption in this case becomes:

$$v_1 n_1(Q) + v_2 n_2(Q) + v_3 n_3(Q) + v_4 n_4(Q) = 0. \qquad (8)$$

$$S_{11}(Q) = < v_1 n_1(-Q).v_1 n_1(Q) > = -S_{12}(Q) - S_{13}(Q) - S_{14}(Q).$$

Note that the spinodal condition is obtained for

$$\text{Det}\left(\underline{\underline{1}} + \underline{\underline{S}}_0(0).\underline{\underline{v}}(0)\right) = 0. \qquad (9)$$

Here $\underline{\underline{1}}$ is the identity matrix and $\text{Det}(...)$ denotes the determinant of a matrix.

3. THE SINGLE-CHAIN FORM FACTORS

The various single-chain form factors for homopolymers and block copolymers are expressed as follows:

$$S_{ii}^0(Q) = n_i \phi_i v_i P_i(Q) \tag{10}$$

$$S_{ij}^0(Q) = \sqrt{n_i \phi_i v_i n_j \phi_j v_j} P_{ij}(Q)$$

$$P_i(Q) = \frac{2}{Q^4 R_{gi}^4} \left[\exp(-Q^2 R_{gi}^2) - 1 + Q^2 R_{gi}^2 \right]$$

$$P_{ij}(Q) = F_i(Q)E_k(Q)F_j(Q) = \left(\frac{1 - \exp\left(-Q^2 R_{gi}^2\right)}{Q^2 R_{gi}^2} \right) \left(\exp(-Q^2 R_{gk}^2) \right) \left(\frac{1 - \exp\left(-Q^2 R_{gj}^2\right)}{Q^2 R_{gj}^2} \right).$$

For Gaussian chains, the radii of gyration are given in terms of the degree of polymerization n_i, and statistical segment lengths a_i as follows:

$$R_{gi}^2 = \frac{n_i a_i^2}{6}. \tag{11}$$

The last expression is better explained through examples. This is done next. Consider examples of block copolymer sequences.
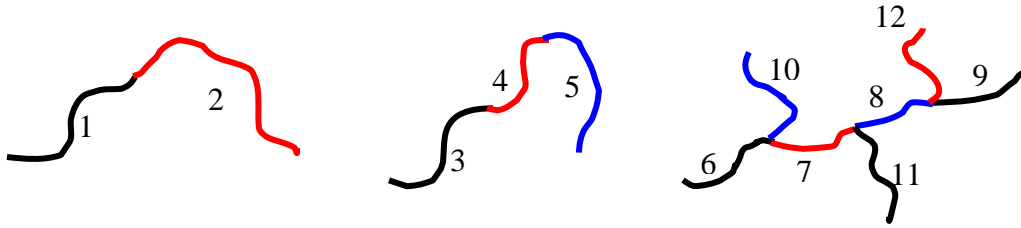

Figure 1: Examples of block copolymer sequences.

F(Q) is used for the two blocks under consideration and E(Q) is used for the blocks in-between. Some inter-block form factors are given here:

$$P_{12}(Q) = F_1(Q)F_2(Q) \tag{12}$$
$$P_{35}(Q) = F_3(Q)E_4(Q)F_5(Q)$$
$$P_{69}(Q) = F_6(Q)E_7(Q)E_8(Q)F_9(Q).$$

These results are valid for Gaussian chains following a random walk (theta condition). For fully swollen chains, the excluded volume parameter approach could be used.

4. BINARY HOMOPOLYMER BLEND MIXTURE

The simplest case to consider is that of a binary blend mixture of two homopolymers (components 1 and 2). In this case, component 2 is taken to be the background component. The results are:

$$S_{11}^0(Q) = n_1 \phi_1 v_1 P_1(Q) \tag{13}$$

$$v_{11}(Q) = \frac{1}{S_{22}^0(Q)} - 2\frac{\chi_{12}}{v_0}$$

$$\frac{1}{S_{11}(Q)} = \frac{1}{S_{11}^0(Q)} + v_{11}(Q)$$

$$S_{11}(Q) = \frac{S_{11}^0(Q)}{1 + v_{11}(Q)S_{11}^0(Q)}.$$

This is the so-called de Gennes formula (De Gennes, 1979) used to describe binary polymer blends in the mixed-phase region.

5. TERNARY HOMOPOLYMER BLEND MIXTURE

The case of a ternary homopolymer mixture is worked out similarly. Component 3 is taken to be the background component. The results are:

$$S_{11}^0(Q) = n_1 \phi_1 v_1 P_1(Q) \tag{14}$$
$$S_{22}^0(Q) = n_2 \phi_2 v_2 P_2(Q)$$
$$S_{33}^0(Q) = n_3 \phi_3 v_3 P_3(Q)$$

$$v_{11}(Q) = \frac{1}{S_{33}^0(Q)} - 2\frac{\chi_{13}}{v_0} \tag{15}$$

$$v_{22}(Q) = \frac{1}{S_{33}^0(Q)} - 2\frac{\chi_{23}}{v_0}$$

$$v_{12}(Q) = \frac{1}{S_{33}^0(Q)} + \frac{\chi_{12}}{v_0} - \frac{\chi_{13}}{v_0} - \frac{\chi_{23}}{v_0}$$

The partial scattering factors for the fully interacting mixture are as follow:

$$S_{11}(Q) = \frac{S_{11}^0(Q)\left(1 + v_{22}S_{22}^0(Q)\right)}{\left(1 + v_{11}S_{11}^0(Q)\right)\left(1 + v_{22}S_{22}^0(Q)\right) - v_{12}^{\ 2}S_{11}^0(Q)S_{22}^0(Q)} \quad (16)$$

$$S_{22}(Q) = \frac{S_{22}^0(Q)\left(1 + v_{11}S_{11}^0(Q)\right)}{\left(1 + v_{11}S_{11}^0(Q)\right)\left(1 + v_{22}S_{22}^0(Q)\right) - v_{12}^{\ 2}S_{11}^0(Q)S_{22}^0(Q)}$$

$$S_{12}(Q) = \frac{-S_{11}^0(Q)v_{12}S_{22}^0(Q)}{\left(1 + v_{11}S_{11}^0(Q)\right)\left(1 + v_{22}S_{22}^0(Q)\right) - v_{12}^{\ 2}S_{11}^0(Q)S_{22}^0(Q)}$$

Recall that the cross section for an incompressible ternary blend mixture is given by (Benmouna et al, 1987; Akcasu-Tombakoglu, 1990):

$$\frac{d\Sigma(Q)}{d\Omega} = \Delta\rho_1^{\ 2}S_{11}(Q) + \Delta\rho_2^{\ 2}S_{22}(Q) + 2\Delta\rho_1\Delta\rho_2 S_{12}(Q). \quad (17)$$

This case applies to a ternary polymer mixture in the homogeneous phase region.

6. BLEND MIXTURE OF A COPOLYMER AND A HOMOPOLYMER

The case of a homopolymer and a copolymer mixture is also readily obtained from the RPA formalism. In this case, the background component is taken to be the homopolymer (component 3). The diblock is formed of components 1-2. The results follow.

$$S_{11}(Q) = \frac{S_{11}^0\left(1 + v_{21}S_{12}^0 + v_{22}S_{22}^0\right) - S_{12}^0\left(v_{21}S_{11}^0 + v_{22}S_{21}^0\right)}{\left(1 + v_{11}S_{11}^0 + v_{12}S_{21}^0\right)\left(1 + v_{21}S_{12}^0 + v_{22}S_{22}^0\right) - \left(v_{11}S_{12}^0 + v_{12}S_{22}^0\right)\left(v_{21}S_{11}^0 + v_{22}S_{21}^0\right)}$$

$$(18)$$

$$S_{22}(Q) = \frac{S_{22}^0\left(1 + v_{12}S_{21}^0 + v_{11}S_{11}^0\right) - S_{21}^0\left(v_{12}S_{22}^0 + v_{11}S_{12}^0\right)}{\left(1 + v_{11}S_{11}^0 + v_{12}S_{21}^0\right)\left(1 + v_{21}S_{12}^0 + v_{22}S_{22}^0\right) - \left(v_{11}S_{12}^0 + v_{12}S_{22}^0\right)\left(v_{21}S_{11}^0 + v_{22}S_{21}^0\right)}$$

$$S_{12}(Q) = \frac{-S_{11}^0\left(v_{11}S_{12}^0 + v_{12}S_{22}^0\right) + S_{12}^0\left(1 + v_{11}S_{11}^0 + v_{12}S_{21}^0\right)}{\left(1 + v_{11}S_{11}^0 + v_{12}S_{21}^0\right)\left(1 + v_{21}S_{12}^0 + v_{22}S_{22}^0\right) - \left(v_{11}S_{12}^0 + v_{12}S_{22}^0\right)\left(v_{21}S_{11}^0 + v_{22}S_{21}^0\right)}$$

The (Q) dependence has been dropped to lighten the notation.

7. THE DIBLOCK COPOLYMER CASE

The RPA result for polymer mixtures containing only copolymers (no homopolymers or solvent) is more complex and will not be included here. It has, however, been worked out

explicitly using a matrix notation and assuming one of the blocks as the background component. The result for the simple case of a diblock copolymer is included here.

$$S_{11}(Q) = \frac{S_{11}^0(Q)S_{22}^0(Q) - S_{12}^0(Q)S_{21}^0(Q)}{\left[S_{11}^0(Q) + S_{22}^0(Q) + 2S_{12}^0(Q)\right] - \frac{2\chi_{12}}{v_0}\left[S_{11}^0(Q)S_{22}^0(Q) - S_{12}^0(Q)S_{21}^0(Q)\right]}. \qquad (19)$$

This is the so-called Leibler formula (Leibler, 1980). This formula can be derived using the linear response approach. Note that the binary blend case is recovered by setting the bare scattering factor cross term $S_{12}^0(Q) = 0$.

8. THE TRIBLOCK COPOLYMER CASE

Consider a triblock copolymer in solution. In our terminology, this is a four "component" case with the triblock as components 1-2-3 and the solvent as component 4. Block 1 is connected to block 2 which is connected to block 3. Block 1 is connected to block 3 only through Block 2 (not directly). Consider component 4 as the "background" component and apply the multi-component RPA formula:

$$\underline{\underline{S_0}}(Q) = \begin{bmatrix} S_{11}^0(Q) & S_{12}^0(Q) & S_{13}^0(Q) \\ S_{21}^0(Q) & S_{22}^0(Q) & S_{23}^0(Q) \\ S_{31}^0(Q) & S_{32}^0(Q) & S_{33}^0(Q) \end{bmatrix}. \qquad (20)$$

In order to work out the various elements $S_{ij}(Q)$, 3*3 matrix inversion and matrix multiplication are needed. The result is too lengthy to reproduce here. The derivation is, however, straightforward (Akcasu et al, 1993).

9. MIXTURE OF POLYELECTROLYTES

Consider a binary mixture containing a charged polymer (polyelectrolyte). The RPA formalism can be adapted to include charge effects. The scattering equations for a binary mixture (where component 1 is a polyelectrolyte) are summarized here (Benmouna-Vilgis, 1991).

$$\frac{1}{S_{11}(Q)} = \frac{1}{S_{11}^0(Q)} + \tilde{v}_{11}(Q) \qquad (21)$$

$$S_{11}(Q) = \frac{S_{11}^0(Q)}{1 + \tilde{v}_{11}(Q)S_{11}^0(Q)}$$

$$\tilde{v}_{11}(Q) = v_{11}(Q) + v_{DH}(Q)$$

$$v_{11}(Q) = \frac{1}{S_{22}^0(Q)} - 2\frac{\chi_{12}}{v_0}$$

$$v_{DH}(Q) = \frac{1}{v_1^2}\frac{4\pi l_B}{Q^2 + \kappa^2}$$

$$\kappa^2 = 4\pi l_B (f\frac{\phi_1}{v_1} + \frac{\phi_{salt}}{v_{salt}}).$$

$v_{DH}(Q)$ is the extra "Debye-Huckel" term that accounts for Coulomb interactions, l_B is the Bjerrum length given by $l_B = \frac{e^2}{\varepsilon k_B T}$, f is the electron charge fraction per monomer and ϕ_{salt} is the salt volume fraction. v_{11} is the interaction factor ($v_1^2 v_{11}$ is the so-called "excluded volume"). As described previously for incompressible neutral polymer mixtures, the scattering cross section for polyelectrolyte mixtures is given by:

$$\frac{d\Sigma(Q)}{d\Omega} = \Delta\rho_1^2 S_{11}(Q) \qquad\qquad (22)$$

$$S_{11}^0(Q) = n_1\phi_1 v_1 P_1(Q)$$
$$S_{22}^0(Q) = n_2\phi_2 v_2 P_2(Q)$$

$$P_1(Q) = \frac{2}{Q^4 R_{g1}^4}\left[\exp(-Q^2 R_{g1}^2) - 1 + Q^2 R_{g1}^2\right].$$

n_1, v_1, ϕ_1, n_2, v_2, ϕ_2, are the degree of polymerization, the specific volume and the volume fraction for components 1 and 2 respectively. $P_1(Q)$ and $P_2(Q)$ are the familiar Debye functions for Gaussian coils. This describes the general case of a polymer blend. If the binary mixture is a polyelectrolyte solution instead, then $n_2 = 1$, $P_2(Q) = 1$ and v_{11} becomes independent of Q.

Consider the following parameters for a polyelectrolyte solution:

f = 0.5   (23)
$n_1 = 1000$
$\phi_1 = 0.04$
$v_1 = 100$ Å^3
$\phi_{salt} =$ either 0.01 (small salt addition) or 0.1 (large salt addition)
$v_{salt} = 100$ Å^3
$l_B = 10$ Å
$v_{11} = 0.05$ Å^{-3}

$R_{g1} = 100$ Å.

The scattering factor $S_{11}(Q)$ is plotted for two salt conditions. The polyelectrolyte peak is observed when small amount of salt is added. When lots of salt is added, the "interaction" peak disappears due to the screening of Coulomb interactions.
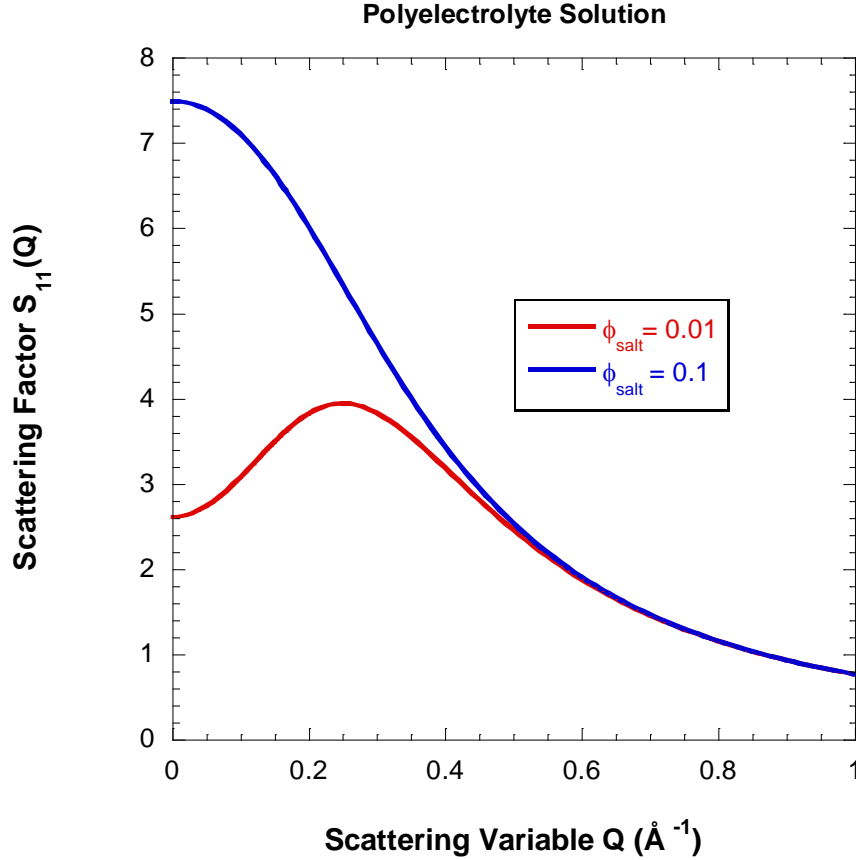
Polyelectrolyte Solution

Figure 2: Variation of the scattering factor $S_{11}(Q)$ for two salt conditions.

The polyelectrolyte interaction peak position obtained corresponds to the maximum in the $S_{11}(Q)$ function. The Debye function is approximated by a simple form and the notation is modified for convenience.

$$P_1(Q) = \frac{1}{1 + \frac{Q^2 R_{g1}^2}{2}} \qquad (24)$$

$$S_{11}(Q) = \frac{S_{11}^0(Q)}{1 + [v_{11} + v_{DH}(Q)]S_{11}^0(Q)} = \frac{F(Q)}{1 + [v_{11} + G(Q)]F(Q)}$$

$$\frac{\partial S_{11}(Q)}{\partial Q} = \frac{F'(Q)}{1 + [v_{11} + G(Q)]F(Q)} - \frac{F(Q)[v_{11}F'(Q) + G'(Q)F(Q) + G(Q)F'(Q)]}{\{1 + [v_{11} + G(Q)]F(Q)\}^2}.$$

The peak position is obtained for the condition:

$$\left[\frac{\partial S_{11}(Q)}{\partial Q}\right]_{Q=Q_{max}} = 0.$$ (25)

This implies:

$$F'(Q_{max}) = F^2(Q_{max})G'(Q_{max})$$ (26)

$$Q_{max}^2 = -\kappa^2 + \sqrt{\frac{n_1\phi_1 8\pi l_B}{v_1 R_{g1}^2}}.$$

The so-called Lifshitz line corresponds to the condition for which the polyelectrolyte interaction peak disappears (i.e., $Q_{max} = 0$).

The spinodal temperature corresponds to the "blowing up" of the scattered intensity; i.e., when the denominator becomes equal to zero.

$$1 + [v_{11} + v_{DH}(Q=0)]S_{11}^0(Q=0) = 0.$$ (27)

The interaction factor v_{11} is plotted as function of salt volume fraction ϕ_{salt}. v_{11} is related to the Flory-Huggins interaction parameter which depends (inversely) on temperature.
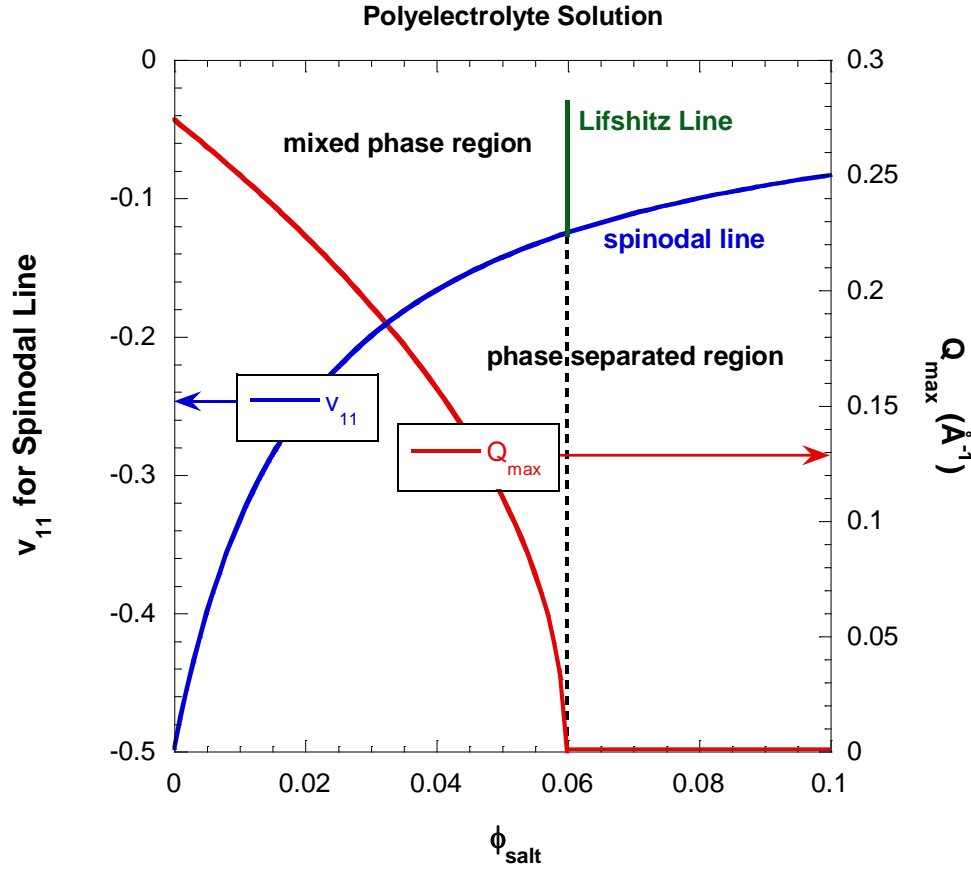
Figure 3: Variation of the interaction factor v_{11} and the of polyelectrolyte peak position Q_{max} with increasing salt volume fraction ϕ_{salt}. The spinodal line and the Lifshitz line are included.

The polyelectrolyte peak feature is due to the modified monomer-monomer interactions that become characterized by two sizes: the actual monomer size and the screened Coulomb interaction distance (represented by κ^{-1}). This produces a "correlation hole" effect. The screened Debye-Huckel interaction potential varies like $V_{DH}(r) \sim \exp(-\kappa r)/r$. Charged interactions tend to stabilize the phase diagram and favor mixing. Adding salt tends to favor demixing. The interaction factor v_{11} is related to the Flory-Huggins interaction parameter χ_{12} which is inversely proportional to temperature. The RPA approach outlined here can apply to more complex polymer mixtures containing polyelectrolytes and neutral polymers.

10. DISCUSSION

The RPA approach described here can handle more complex polymer mixtures containing complex architectures and blockiness (Hammouda, 1993). It amounts to inverting and multiplying larger matrices. The effect of chain stiffness has also been included in limited cases. Mixtures of flexible and stiff polymer chains are characterized by the familiar spinodal condition as well as by the isotropic-to-nematic phase transition (Hammouda, 1993).

It should be emphasized, however, that this mean-field approach applies strictly in the mixed-phase region (not too close to the phase boundary line). Non-mean field corrections have been worked out. These are, however, outside the scope of this effort.

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QUESTIONS

1. Write down the generalized Random Phase Approximation formula for multi-component incompressible polymer mixtures. Does it apply to pure copolymers?

2. Write down the scattering cross section for a multi-component polymer mixture of arbitrary composition in matrix form.
3. What is the size of the matrix to be inverted for an incompressible mixture with four polymer components?
4. Write down the so-called de Gennes formula for scattering from a binary polymer blend mixture. Define the various terms.
5. Write down the $S_{11}(Q)$ interacting scattering factor for a ternary polymer blend mixture.
6. Write down the so-called Leibler formula for scattering from a diblock copolymer.
7. Stiff (rodlike) polymers are characterized by orientational phase transitions beside the spinodal and binodal lines. Name the two best known phase transitions.
8. What is the extra interaction term which is added to account for screened charge-charge interactions and thereby extend the multicomponent RPA approach to included polyelectrolytes?

ANSWERS

1. The Random Phase Approximation general formula for multi-component incompressible polymer mixtures expresses the fully interacting scattering factor $\underline{\underline{S}}(Q)$ in terms of the "bare" (non-interacting) scattering factor $\underline{\underline{S}}_0(Q)$ and the various interaction factors $\underline{\underline{v}}(Q)$ as $\underline{\underline{S}}^{-1}(Q) = \underline{\underline{S}}_0^{-1}(Q) + \underline{\underline{v}}(Q)$. This does not apply to pure copolymers since a "background" component (either a homopolymer or a solvent) is required.

2. The scattering cross section for a multi-component polymer mixture of arbitrary composition is expressed as $\dfrac{d\Sigma(Q)}{d\Omega} = \vec{\rho}^{\,T}\underline{\underline{S}}(Q).\vec{\rho}$ where $\vec{\rho}$ is a column vector containing all of the scattering length densities and $\underline{\underline{S}}(Q)$ is a matrix containing all of the scattering factors.

3. A homogeneous polymer mixture with four components generates a 3*3 RPA matrix to be inverted. The fourth component is taken to be the background component.

4. The de Gennes formula for scattering from a binary polymer blend mixture is expressed as $\dfrac{1}{S_{11}(Q)} = \dfrac{1}{S^0_{11}(Q)} + \dfrac{1}{S^0_{22}(Q)} - \dfrac{2\chi_{12}}{v_0}$. Here $S^0_{11}(Q)$ and $S^0_{22}(Q)$ are the bare scattering factors, χ_{12} is the Flory-Huggins interaction parameter and v_0 is a reference volume usually expressed as $v_0 = \sqrt{v_1 v_2}$ where v_1 and v_2 are the specific monomer volumes.

5. The scattering factor for a ternary polymer blend mixture is given by
$$S_{11}(Q) = \dfrac{S^0_{11}(Q)\left(1 + v_{22}S^0_{22}(Q)\right)}{\left(1 + v_{11}S^0_{11}(Q)\right)\left(1 + v_{22}S^0_{22}(Q)\right) - v_{12}^{\;2}S^0_{11}(Q)S^0_{22}(Q)}$$. The various factors are defined in the text.

6. The Leibler formula is expressed as $S_{11}(Q) = W(Q)\Big/\left[S(Q) - \dfrac{2\chi_{12}}{v_0}W(Q)\right]$ where

$W(Q) = S^0_{11}(Q)S^0_{22}(Q) - S^0_{12}(Q)S^0_{21}(Q)$ and $S(Q) = S^0_{11}(Q) + S^0_{22}(Q) + 2S^0_{12}(Q)$.

7. Stiff polymers are characterized by the spinodal and binodal temperatures as well as orientational transitions leading from the isotropic to the nematic or smectic phases.

8. The extra interaction term added to extend the multicomponent RPA approach to include polyelectrolytes is the Debye-Huckel factor $v_{DH}(Q) = \dfrac{1}{v_1^2}\dfrac{4\pi l_B}{Q^2 + \kappa^2}$ where v_1 is

the monomer volume, κ^{-1} is the screening length, and l_B is the Bjerrum length given by

$l_B = \dfrac{e^2}{\varepsilon k_B T}$.